CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 Introduction

The nanopowders of ceramic materials obtained through the present combustion process are crystalline and dielectric in nature. The structure, phase purity and thermal stability of the materials are studied by X-ray diffraction technique, differential thermal analysis, thermo gravimetric analysis and FT-Raman and FT-IR spectroscopy. The particle morphology of the nanopowders is studied by transmission electron microscopy. The dielectric properties of the sintered pellets of the nanomaterials are studied by LCR meter. The suitability of the materials prepared through the combustion method as substrate material for high Tc superconducting films is carried out by temperature-resistance measurements using four-probe technique. The details of different characterization techniques used in the present work are discussed in this chapter.

Combustion synthesis is a novel technique to prepare nanopowders in a simple and straightforward method. In the present work Ba$_2$RESbO$_6$ (RE = Y, Sm, Gd, Dy) ceramic materials are prepared by the modified combustion method. In this method, aqueous solution of the constituent ions of Ba, RE and Sb are prepared by dissolving stoichiometric amounts of respective nitrates /oxides /tartarates. These solutions are mixed together and an equivalent quantity of citric acid is added. The amount of citric acid is kept at the citric acid to cation ratio unity. The oxidant/fuel ratio of the system is adjusted by the addition of nitric acid and ammonium hydroxide. The solution containing the complex precursor at neutral pH is then heated in a hot plate. Initially the solution
boils and on completion of evaporation the solution turns into foam. The foam then
ignites and the product of combustion is voluminous and fluffy.

2.2 Powder X-Ray Diffraction Technique

The structure of the nano powdered ceramic specimens in this investigation is
analyzed by X-Ray Diffraction (XRD) techniques. The powder X-Ray diffraction method
is one of the most important tools for the qualitative analysis of materials. An X-Ray
diffractometer utilizes a powdered sample, a goniometer, and a fixed-position detector to
measure the diffraction patterns of unknown powdered materials.

The powdered sample provides (theoretically) all possible orientations of the
crystal lattice, the goniometer provides a variety of angles of incidence, and the detector
measures the intensity of the diffracted beam. The diffracted X-rays from individual
crystallites that happen to be oriented with the planes making an incident angle with the
beam satisfies Bragg’s equation

\[ n\lambda = 2dsin\theta \]  

(2.1)

where, \( \lambda \) is the wavelength of the incident radiation, \( n \) is the order of the spectrum
and \( d \) is the interplanar spacing. The resulting analysis is described graphically as a set of
peaks with percentage intensity on the Y-axis and goniometer angle on the X-axis. The
exact angle and intensity of a set of peaks is unique to the crystal structure being
examined [1]. A monochromator is used to ensure a specific wavelength reaches the
detector, eliminating fluorescent radiation. The resulting trace consists of a recording of
the intensity against counter angle (2\( \theta \)). The trace can then be used to identify the phases
present in the sample. Diffraction data from many materials have been recorded in a
computer searchable Powder Diffraction File (PDF/JCPDS File). Comparing the observed data with that in the PDF, allows the phases in the sample to be identified [2].

In the present investigation, XRD spectra are recorded using a computerized X-ray Diffractometer (Model Bruker D-8) with Nickel filtered Cu-Kα radiation. Identification of the phases is done by comparing the d spacings and line strengths of the observed X-ray diffraction pattern of the sample with the standard reference data.

2.3 Differential Thermal Analysis (DTA)

Differential thermal analysis is a thermal technique in which the temperature of a sample, compared with the temperature of a thermally inert material, is recorded as a function of the sample, inert material, or furnace temperature as the sample is heated or cooled at a uniform rate. Temperature changes in the samples are due to endothermic or exothermic enthalpic transitions or reactions such as those caused by phase changes, fusion, crystalline structure inversions, boiling, sublimation and vaporization, dehydration reactions, dissociation or decomposition reactions, oxidation and reduction reactions, destruction of crystalline lattice structure and other chemical reactions. Generally, phase transitions, dehydration, reduction, and some decomposition reactions produce endothermic effects, whereas crystallization, oxidation, and some decomposition reactions produce exothermic effects. The temperature changes occurring during these chemical or physical changes are detected by a differential method as shown in figure 2.1. If the sample and reference temperatures are Ts and Tr, respectively, then the difference in temperature, Ts-Tr is the function recorded.
A typical DTA curve is illustrated in figure 2.2. Four types of transitions are illustrated: (1) second order transition in which a change in the horizontal base line is detected (2) an endothermic curve peak caused by a fusion or melting transition (3) an endothermic curve peak due to a decomposition or dissociation reaction and (4) an exothermic curve peak caused by a crystalline phase change. The number, shape, and position of the various endothermic and exothermic peaks with reference to the temperature may be used as a means for the qualitative identification of the substance under investigation. Also, since the area under the peak is proportional to the heat change involved, the technique is useful for the semi quantitative or in some cases quantitative determination of the heat of reaction. Since the heat of reaction is proportional to the amount of reacting substance, DTA can be used to evaluate quantitatively the amount of substance present if the heat of reaction is known.
2.4 Thermo-Gravimetric Analysis (TGA)

The thermal analysis technique of Thermo-Gravimetry (TG) is one in which the change in sample mass (mass-loss or gain) is determined as a function of temperature and/or time. Three modes of thermogravimetry is commonly used as illustrated in figure 2.3: (a) isothermal thermogravimetry in which the sample mass is recorded as a function of time at constant temperature (b) quasi-iso-thermal temperature thermogravimetry in which the sample is heated to constant mass at each of a series of increasing temperatures and (c) dynamic thermogravimetry in which the sample is heated in an environment whose temperature is changing in a predetermined manner, preferably at a linear rate. Most of the studies discussed here will refer to dynamic thermogravimetry, which will be designated as thermogravimetry.
Figure 2.3: Three modes of thermogravimetry (a) Isothermal thermogravimetry (b) quasi-isothermal thermogravimetry (c) dynamic thermogravimetry [3].
The resulting mass-change versus temperature curve provides information concerning the thermal stability and composition of the initial sample, the thermal stability and composition of any intermediate compounds that may be formed, and the composition of the residue, if any.

In the present study simultaneous Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) are carried out using Perkin-Elmer TG/DT thermal analyzer in the range 30 - 1000 °C at a heating rate of 20 °C/min in nitrogen atmosphere to study the chemical stability of the as prepared materials with the increase in temperature.

2.5 FT-IR Spectroscopy

FT-IR (Fourier Transform Infrared) Spectroscopy is a technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. It is used to identify unknown materials present in a specimen. The principle of this technique lies in the fact that when IR interacts with the materials, various chemical bonds in the material vibrate as it absorbs the IR radiation. These vibrations are either in the stretching or in the bending mode. When infrared light is passed through a material some of the frequencies are absorbed while other frequencies are transmitted through the sample without being absorbed. Analysis of the transmitted light reveals how quantum of energy is absorbed at each wavelength, which can be done using a Fourier transform instrument by measuring all the wavelengths at once [4].

The Infrared (IR) spectra of the samples are recorded in the range 400 - 4000 cm\(^{-1}\) on a Thermo-Nicolet Avatar 370 Fourier Transform Infrared (FTIR) spectrometer. The materials are finely dispersed in KBr using an agate mortar and ground well. The finely
dispersed material is then pressed in the form of circular discs of ~10 mm diameter and 0.5 mm thickness at a pressure 250 MPa. These pellets are then dried with IR light before the FT-IR spectrum has been recorded.

2.6 FT-Raman Spectroscopy

Raman spectroscopy deals with scattering of light and not with its absorption. Homonuclear diatomic molecules such as H₂, N₂, O₂, etc. which do not show IR spectra since they do not possess a permanent dipole moment do show Raman spectra since their vibration is accompanied by a change in polarisability of the molecules. As a consequence of the change in polarisability there occurs a change in the induced dipole moment at the vibrational frequency. Many molecules have modes that are IR active and other modes that are Raman active. Raman spectroscopy thus permits us to examine the vibrational spectra of compounds that do not lend themselves to IR spectroscopy. Raman spectroscopy uses visible or ultraviolet radiation rather than infrared radiation. Hence, the walls of the sample cell and other units of the optical system can be made of glass or quartz rather than of special materials that are transparent to IR radiation.

Principle

Photons can interact with molecules of matter in number of ways. When they strike a solid or collection of molecules, most of them are scattered elastically (Rayleigh scattering). But a few (1 in 10⁶) undergo inelastic scattering. These inelastically scattered photons have frequencies lower and higher than the incident frequency. This phenomenon, predicted in 1923 by Smekel and observed by Sir.C.V.Raman in 1928, is referred to as Raman scattering. The lines on the low and high frequency sides of the Rayleigh line are called stokes and anti-stokes lines, respectively (figure 2.4).
Figure 2.4: The illustration for different cases of scattering

The stokes and anti-stokes line are found to be symmetrical with respect to Rayleigh line. The frequency difference of each Raman line from Rayleigh line is called Raman frequency. The stokes line is found to be more intense than anti-stokes lines. This is because anti-stokes Raman scattering involves transition to a lower state from a populated higher energy state. The scattered photons have frequency shifts 10-4000 cm\(^{-1}\) characteristic of the vibrational and rotational energies of the molecule. These weak lines of modified frequencies are generally referred to as Raman spectrum and the frequency shift from the exciting line as Raman shift.

Conventional Raman spectroscopy measures intensity versus frequency or wavenumbers, while, FT Raman instruments measure the intensity of light of many frequencies simultaneously. This spectrum is then converted into a conventional spectrum by means of Fourier transformation using computer algorithm. The distinctive feature of the FT technique is that information for all the wavelengths falls on the
detector at all times. This provides improved resolution, spectral acquisition times, and S/N ratios over conventional dispersive Raman spectroscopy.

FT-Raman instruments employ a CW Nd: YAG laser with an excitation at 1064 nm (Figure 2.5) and the important aspect of FT-Raman instrumentation is the necessity for optical filtering. The filtering must be capable of reducing the Rayleigh line which is $10^6$ stronger than the stokes-shifted lines in the Raman spectrum. Holographic notch filters have been successful in eliminating light at laser frequency from the scattered signal. These filters are fabricated by recording interference patterns formed between two mutually coherent laser beams on multiple film layers.

2.7 The Transmission Electron Microscope (TEM)

The transmission electron microscope (TEM) uses electrons as "light source" and their much lower wavelength makes it possible to get a resolution a thousand times better
than with a light microscope. The possibility for high magnifications has made the TEM a valuable tool in both medical, biological and materials research.

The working of the transmission electron microscope is shown in figure 2.6. An "electron source" at the top of the microscope emits the electrons that travel through vacuum in the column of the microscope. Instead of glass lenses focusing the light in the light microscope, the TEM uses electromagnetic lenses to focus the electrons into a very thin beam. The electron beam then travels through the specimen to be studied. Depending on the density of the material present, some of the electrons are scattered and disappear from the beam. At the bottom of the microscope the unscattered electrons hit a fluorescent screen, which gives rise to a "shadow image" of the specimen with its different parts displayed in varied darkness according to their density. The image can be studied directly by the operator or photographed with a camera.

Figure 2.6: Picture showing the working of TEM
Sample preparation

In material science/metallurgy the specimens tend to be naturally resistant to vacuum, but must be prepared as a thin foil or etched so that some portion of the specimen is thin enough for the beam to penetrate. Preparation techniques to obtain an electron transparent region include ion beam milling and wedge polishing. The focused ion beam (FIB) is a relatively new technique to prepare thin samples for TEM examination from larger specimens. Because the FIB can be used to micro-machine samples very precisely, it is possible to mill very thin membranes from a specific area of a sample, such as a semiconductor or metal. Materials that have dimensions small enough to be electron transparent, such as powders or nanotubes, can be quickly produced by the deposition of a dilute sample containing the specimen onto support grids. The suspension is normally a volatile solvent, such as ethanol, ensuring that the solvent rapidly evaporates allowing a sample that can be rapidly analysed.

For the present study, powders obtained through the combustion synthesis are examined using transmission electron microscopy (TEM, Model: PHILIPS- CM 200, resolution 2.4 Å) at operating 200 kV. The samples for Transmission Electron Microscope (TEM) are prepared by ultrasonically dispersing the powder in methanol and allowing a drop of this to dry on a carbon-coated copper grid.

Transmission Electron Microscopy (TEM) is widely used to characterize a lot of materials both from a morphological point of view and from the crystallographic but also for the elemental composition. Using TEM a large variety of materials as ceramics, minerals, metals, alloy, semiconductors, glass and polymers can be observed. The main
requirements for the samples are: due to the high vacuum ambient of work they must not outgass and they have to be appropriately thinned to be observed.

2.8 Shaping

Depending on the shape and required characteristics, numerous powders shaping process have been developed. The most commonly used powder shaping techniques are die pressing, rubber mold pressing, extrusion molding, slip casting and injection molding [5]. The powder itself consists of solid brittle particles, so it is difficult to fill the powder in a die by pressure alone. As the pressure is increased, there is more strain on the compact, and cracks that can cause the compact to fracture are formed. Therefore a binder like polyvinyl alcohol is usually added to enhance the fluidity of the powder [6]. Polyvinyl alcohol is the commonly used binder for the forming of oxide ceramics. In the present study, the powders are mixed with 5% polyvinyl alcohol and are uniaxially pressed at a pressure of ~ 350 MPa using a hydraulic press.

2.9 Sintering

Sintering is the most important step during ceramic processing, because it is at this stage that a powder compact is exposed to temperature. When a ceramic material is heated, there is a certain temperature at which they begin to diffuse, and in most cases there is shrinkage resulting in densification. During this process, the redistribution of matter takes place in such a way that minimizes the system free energy. Besides densification many electrical, magnetic, optical and mechanical properties are determined by the physical and chemical changes during sintering at high temperature. Characteristics of the sintering powder such as particle size distribution, degree of particle agglomeration, particle shape, shape distribution, particle aggregates, have a
profound influence on densification and microstructural development [7]. A large number of sintering methods such as standard pressure sintering, hot pressing, hot isostatic pressing, reaction sintering, recrystallization sintering, ultra high pressure sintering are frequently employed [5].

2.9.1 Nano sintering

Attempts to consolidate nanoscale powders by conventional sintering methods have been frustrated by the inability to retain an ultra-fine grain size in the fully sintered products. This is because the presence of an unusually high interface area between grains provides a strong driving force for grain growth. For certain nanomaterial applications, sintering of powders while retaining grain sizes in the nanometer range become a critical processing step. Fully dense specimens with nanosize features are most important for structural, magnetic, electric or electronic applications. The main focus in the consolidation of out-of-equilibrium powders has been the retention of the metastable condition of the initial structures. The inevitable coarsening tendency and small specimen size produced by nanopowder densification generated at least some controversies on nanomaterial properties. Consolidation of nanopowders has been summarized in a number of recent reviews [8, 9]. Nanosintering presents additional challenges as compared to sintering of regular powders due to particle agglomeration, high reactivity and inherent contamination, grain coarsening and ultimate loss of the nanofeatures.

High green densities are necessary to avoid large grain growth during densification. On the other hand lower green densities in the green compact are tolerable if pressure is applied in the densification process. A problem that arises during the densification of all nanophase powders is grain growth. Accelerated grain growth is
observed in most nanophase materials systems when the density exceeds about 90% TD. A major problem in the processing of nanophase oxide powders is the existence of agglomerates in these powders and as a result the formation of relatively large interagglomerate pores during pressing (Figure 2.7).

![Figure 2.7: Schematic diagram of an agglomerated powder (Mayo [10])](image)

While small interparticle pores are easily closed during sintering, large interagglomerate pores need high sintering temperatures or long sintering times. Pores exceeding a critical size will even grow during sintering. Hence significant grain growth will take place. One possible way to overcome this problem is the use of sinter forging techniques. In this process the large pores can be closed by the plastic deformation of the ceramic and as a result finer grain size values can be obtained [10]. Mayo developed a modified sintering law that directly accounts for pore size effects on densification rate [8]:

$$\frac{1}{\rho(1-\rho)} \frac{dp}{dt} \propto \frac{1}{D^n} \exp \left( \frac{-Q}{RT} \right)$$

(2.2)
Where, \( p \) is density, \( d \) is the particle size, \( n \) is a constant dependent on the sintering mechanism, \( r \) is the pore radius, \( Q \) is the activation energy, \( R \) is the gas constant and \( T \) is the absolute sintering temperature. This equation predicts that the highest densification rate occurs for the finest pore size. Thermodynamically, powders are unstable due to large surface area. Nanoparticles adopt different surface energies than regular ones, for instance, by a different local atomic arrangement at the surface. Kinetically, sintering of nanopowders is significantly enhanced. Full densification of nanopowders is completed at temperatures lower than that for conventional powders, as well.

There has been extensive effort to fabricate nanostructured ceramics. Methods such as hot-pressing, hot isostatic pressing, spark plasma sintering etc. have been employed. Conventional pressureless sintering is the most common low cost approach to sinter ceramics but it is difficult to realize densification without grain growth. This has stimulated researchers to develop new consolidation methods. Duan et al [11] demonstrated the preparation of \( \text{Al}_2\text{O}_3/\text{TiO}_2 \) nanocomposite by high pressure sintering where addition of nano-MgO powder improved the densification and retarded grain growth. The grains are on the order of 100 nm. The nanocomposite contains grains of alumina, titania, and magnesia. Although the pressure (~1 GPa) and temperature (~850 °C/30 min) are high, no significant grain coarsening occurred because of the different compositions. Kear et al [12] developed two production methods, one method called transformation assisted consolidation (TAC) and the other plasma spraying to consolidate nanocrystalline powder without grain growth. Densification of pure nano crystalline MgO powder with 10 nm particle size by hot-pressing was investigated by Ehre et al [13] in the temperature range 700–800 °C, applied pressure range
100–200 MPa, and for duration of up to 240 min. Luan et al [14] obtained fine-grained BaTiO$_3$ ceramic at a low sintering temperature of 900 °C within a short sintering period by means of a new sintering technique called Spark Plasma Sintering (SPS). The ceramic was shown to be highly densified to more than 99% of the theoretical density with homogeneous microstructures, signifying that the SPS process is effective for densification. Lee et al [15] investigated the effect of spark plasma sintering on the densification of TiO$_2$ ceramics. A fully-dense TiO$_2$ specimen with an average grain size of ~200 nm was reported by spark plasma sintering at 700 °C for 1 h.

For the present study the as-prepared nano powders are mixed with 5% polyvinyl alcohol and pressed in the form of cylindrical pellets of 14 mm diameter and ~2mm thickness at a pressure about 350 MPa using a hydraulic press. The pellets are sintered by conventional method by heating at high temperatures in a programable furnace. The bulk densities of the sintered samples are measured using the Archimedes method.

2.10 The Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. A beam of electrons is generated in the electron gun, located at the top of the column, which is pictured to the left as shown in figure 2.8. This beam is attracted through the anode, condensed by a condenser lens and focused as a very fine point on the sample by the objective lens. The scan coils are energized (by varying the voltage produced by the scan generator) and create a magnetic
field which deflects the beam back and forth in a controlled pattern. The varying voltage is also applied to the coils around the neck of the Cathode-Ray Tube (CRT) which produces a pattern of light deflected back and forth on the surface of the CRT. The pattern of deflection of the electron beam is the same as the pattern of deflection of the spot of light on the CRT. The electron beam hits the sample, producing secondary electrons from the sample. These electrons are collected by a secondary detector or a backscatter detector, converted to a voltage and amplified. The amplified voltage is applied to the grid of the CRT and causes the intensity of the spot of light to change. The image consists of thousands of spots of varying intensity on the face of a CRT that correspond to the topography of the sample.

The SEM requires that specimens be conductive for the electron beam to scan the surface and that the electrons have a path to ground. All samples must also be trimmed to an appropriate size to fit in the specimen chamber and generally mounted on some sort of holder. Metals require little special preparation for SEM except for mounting on an appropriate specimen holder. Nonconductive solid specimens are coated with a layer of conductive material, except when observed with variable vacuum or environmental SEMs. An ultrathin coating of electrically-conducting material such as, gold, gold/palladium alloy, platinum, tungsten or graphite is deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. This is done to prevent the accumulation of static electric charge on the specimen during electron irradiation. Another reason for coating even when there is more than enough conductivity is to improve contrast and resolution. There are many advantages of using the SEM instead of a light microscope. The SEM has a large depth of field which allows a large amount of
the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

The spatial resolution of the SEM depends on the size of the electron spot, which

![Figure 2.8: Schematic diagram showing working of SEM](image)

in turn depends on both the wavelength of the electrons and the magnetic electron-optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. The spot size and the interaction volume both might be large compared to the distances between atoms, so the resolution of the SEM is not high enough to image
individual atoms, as is possible in the shorter wavelength (i.e. higher energy) transmission electron microscope (TEM).

2.11 Dielectric measurements

At low frequencies, the determination of dielectric constant is usually based on the measurement of capacitance of a parallel plate capacitor or coaxial capacitor containing the material under test. The technique is based on the principle that when a material is introduced between the plates of a parallel plate capacitor, its capacitance increases by a factor $\varepsilon_r$, the dielectric constant of the material. The dielectric constant $\varepsilon_r$ is related with the capacitance $C$ as

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$$ (2.3)

where, $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-12} \text{ F/m}$), $A$ is the area of the disc and $d$ is the thickness of the specimen.

The dielectric constant $\varepsilon_r$ and loss factor ($\tan \delta$) of the materials have been studied using LCR meter (Hioki-3532-50) in the frequency range 100Hz–3 MHz at room temperature. The materials used for the dielectric measurements are sintered to high density (>96%) in the form of circular discs of diameter ~10 mm and thickness ~1 mm. The sintered specimens are mechanically polished and cleaned the surfaces and are dried in an electric oven at a temperature of ~100 °C for 4h. Copper leads are taken from the silver electrode surfaces. This is used as the sample for dielectric measurements. The capacitance and dissipation factors are directly measured from the LCR meter at room temperature. Knowing the capacitance value the dielectric constant of the material is determined using the above equation.
2.12 Thermal Diffusivity: Photothermal Deflection Spectroscopy (PDS) technique

Photothermal approach to measure transport processes is based on the principle of optical beam deflection. Significant advantage of this technique over other electrical measurements is that it is contactless and directly yields thermal diffusivity of the bulk specimen [16]. Excitation (or pump) beam used in the present Photothermal Deflection Spectroscopy (PDS) technique is a continuous laser beam ($\lambda = 532$ nm) from a semiconductor diode pumped Nd-YAG laser (CASIX) of power 25 mW, which is modulated using a mechanical chopper (model SR 540). Figure 2.9 shows the experimental setup.

![Figure 2.9: Schematic of photothermal deflection experimental set up.](image)

The modulated pump beam is directed perpendicular to the sample surface. Energy absorbed is converted to heat due to non-radiative processes in the material. Heat thus generated, flows to the surrounding medium in which a modulated refractive index gradient is generated. Another probe laser beam, passing close and parallel to the sample surface through this refractive index gradient, experiences deflection of amplitude ($\tilde{\delta}$).
from its path [17]. In condensed phase measurements, PDS technique is often limited by noise [18]. Noise sources that determine sensitivity of this technique are mechanical vibrational pickup, motion of the fluid in which the refractive index is created, and oscillating intensity of the laser beam. In order to increase signal to noise ratio (S/N), the sample is placed within a sample cell filled with double-distilled carbon tetrachloride (CCl₄) solution. The whole setup is mounted on a vibration isolation table. Photo thermal data was recorded only after the intensity of laser beam was stable. Detector electronic noise also affects the sensitivity. Hence a low noise-high gain operational amplifier (OPA111-Burr Brown) is used in an instrumentation amplifier circuit. A Bi-cell photodiode (EG & GUV-140 BQ-2) is used to measure the deflection. This amplified signal is then fed to a dual input lock-in-amplifier (SR 830) to collect the phase and amplitude of the thermal wave generated. All the samples are characterized in this in-house built photo thermal deflection setup. An intensity modulated light beam generates periodic thermal wave due to optical heating. Thermal wave, otherwise called as 'diffusion wave', generated will propagate into solid and the surrounding media according to usual diffusion process, creating a thermal gradient. The wave-like disturbances involve oscillations of diffusing energy or particles [19]. Their generation and detection in condensed matter form the basis of the measurement and understanding of optical, electronic and thermal properties of the material. In 1861, Angstrom initiated the study on diffusion waves. He calculated thermal diffusivity of solids using diffusion waves. The value of thermal diffusivity (α) is determined from the slope of the plot of logarithm of the PDS signal verses the square root of the chopping frequency, using the following relation [20]
\[ \alpha = \pi \left( \frac{l}{\text{slope}} \right)^2 \quad (2.4) \]

where \( l \) is the thickness of the sample.

### 2.13 Vickers Microhardness

Hardness is one of the most frequently measured properties of a ceramic. Its value helps to characterize resistance to deformation, densification, and fracture. Hardness is crucial for cutting tools, wear and abrasion-resistant parts, optical lens glasses, ballistic armor, molds and dies, valves, and seals. In fact, many ceramic specifications list minimum hardness requirements. The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a load of 1 to 100 kgf as shown in figure 2.10. The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is the quotient obtained by dividing the kgf load by the square mm area of indentation.

\[ F = \text{Load in kgf} \]
\[ d = \text{Arithmetic mean of the two diagonals, } d_1 \text{ and } d_2 \text{ in mm} \]
\[ H_v = \text{Vickers hardness} \]
\[ H_v = \frac{2F \sin \frac{136^0}{2}}{d^2} \quad (2.5) \]

When the mean diagonal of the indentation has been determined the Vickers hardness may be calculated from the formula. The Vickers hardness should be reported like 800HV/10, which means a Vickers hardness of 800 is obtained using a 10 kgf force.
Figure 2.10: Schematic diagram of diamond indenter, in the form of a right pyramid with a square base

The Vickers microhardness measurements of sintered samples are carried out at room temperature using microhardness tester.

2.14 Resistance measurements

Superconducting property of the material can be characterized by measuring the resistance of the sample. The superconducting transition temperature (Tc) can be directly determined by resistance measurements of the sample as a function of temperature. In the present study, standard four-point probe method is used for the resistance measurements of the superconductor and superconducting thick film samples. The four-probe method of measuring the resistance has the advantage over two-probe method that the effects due to contact resistance, lead resistance etc can be avoided.

Four probe technique in van der Pauw geometry permits the measurement of an isotropic sample of uniform flat thickness but with arbitrary shape if meet the following
criteria [21, 22]. The different criteria are: (i) the contacts are at the periphery of the sample (ii) the contacts are sufficiently small (iii) the sample is uniform in thickness, (iv) the sample does not contain holes and (v) the sample is homogeneous. The measurement is based on a theorem, proved by van der Pauw [21, 22], for a sample of uniform thickness and for arbitrary shape with four arbitrarily positioned contacts (A, B, C & D) on the edges as shown in figure 2.11.

![Figure 2.11: Lead arrangement for van der Pauw with four contacts A, B, C and D on the periphery for resistance measurements](image)

If we define

$$R_{AB,CD} = \frac{V_D - V_C}{I_{AB}}$$  \hspace{1cm} (2.6)

and

$$R_{BC,DA} = \frac{V_A - V_D}{I_{BC}}$$  \hspace{1cm} (2.7)

where $V_D - V_C$ is the potential difference between contacts D and C caused by the passage of current I from A to B, etc. van der Pauw theorem takes the form

$$\exp(-\pi R_{AB,CD} d / \rho) + \exp(-\pi R_{BC,DA} d / \rho) = 1$$  \hspace{1cm} (2.8)

Where $\rho$ is the resistivity and d is the sample thickness. This equation can be solved for $\rho$, we get
\[ \rho = \left( \frac{\pi d}{\ln 2} \right) \{ (R_{AB,CD} - R_{BC,DA}) / 2 \} \{ F(R_{AB,CD}) / (R_{BC,DA}) \} \]  

(2.9)

Here \( F \) is a function of the ratio of resistance such that

\[ (R_{AB,CD} - R_{BC,DA}) / (R_{AB,CD} + R_{BC,DA}) = F \cosh\{ \exp(\ln 2 / F) \} / 2 \]  

(2.10)

In the special case of samples and constants which are in variant under rotation of 90°, the sheet resistance \( R_s = \rho / d \) reduces to simple form

\[ R_s = (\rho / \ln 2)(V / I) = (\pi / \ln 2) R_{AB,CD} = (\pi / \ln 2) R_{AC,BD} \]  

(2.11)

specimens with such symmetry are often easily prepared. Here \( V \) is the voltage between two voltage contacts and \( I \) is the current flowing through two current contacts. The resistivity measurements can be made with either direct or alternating current. With direct current care must be taken to eliminate the effects of thermoelectric voltages in the voltage circuit by frequency reversing the sample current.

In the present study conventional four-probe DC resistance method is utilized for Resistance vs temperature measurement in sintered bulk pellets. For making contacts the surface of bulk pellets are freshly prepared by scratching their surface with a razor blade. Four tiny spots are made in a linear configuration on the pellets by applying conductive silver paste. Pasted pellets are dried at room temperature and subsequently cured at 300 °C for about 30 minutes prior to soldering the leads. Thin copper wires are connected to the contacts by soldering. Outer two leads are meant for current and a constant current of 10 mA is used for resistance measurement of bulk pellets. The voltage drop between the inner two leads is measured using a programmable nano voltmeter. The temperature of the sample is monitored by a temperature controller (Lakeshore model: L340) using a temperature sensor. The measurements are taken from 300 K to 77 K in a variable
temperature liquid nitrogen (LN$_2$) cryostat and the temperature is varied slowly by lowering the sample holder in the cryostat. The schematic diagram of the sample holder used is shown in Fig. 2.12.

Figure 2.12: Sample holder set up to measure the electrical resistivity of the sample
REFERENCES


